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Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std. 239.18

MEMORANDUM FOR PRR (Contractor/In-House Publication)

FROM: PROI (TI) (STINFO)

1 June 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0110

Fajardo and Tam, "High Resolution Infrared Absorption Spectroscopy of Molecular Dopants in Cryogenic Solid Parahydrogen"

Poster Session HEDM CONFERENCE

(Public Release)

High Resolution Infrared Absorption Spectroscopy of Molecular Dopants in Cryogenic Solid Parahydrogen

Mario E. Fajardo and Simon Tam
US Air Force Research Laboratory, Propulsion Directorate
(AFRL/PRSP Bldg. 8451, Edwards AFB, CA 93524-7680) mario_fajardo@ple.af.mil

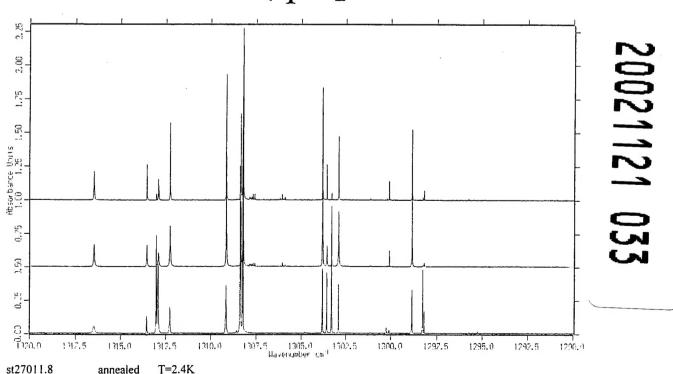
Premature claims of successful energy storage in cryogenic solids date back to the National Bureau of Standards' Free Radicals program. Such errors typically result from reliance on unsupplemented calorimetric data, which shed little light on the mechanism of energy storage, i.e. chemical identities of the energetic species and microscopic structures within the trapping medium. Only spectroscopic measurements provide the species and structure specific information required for directed incremental progress towards higher stored energy densities.

In HEDM program funded studies, Oka and co-workers pioneered the use of high resolution spectroscopic techniques in solid parahydrogen (pH₂). Our rapid vapor deposition sample preparation technique now enables us to trap virtually any volatilizable species in solid pH₂. We present results of high resolution infrared absorption experiments on pH₂ solids doped with isolated molecules and small clusters.

DISTRIBUTION STATEMENT A

Approved for Public Release Distribution Unlimited

13 PPM CH₄/pH₂ d≈3mm



st27011.8 st27011.4 st27011.2 annealed Tannealing Ta

annealing T=4.8K as deposited T=2.4K

resolution = 0.0075 cm^{-1}

OBJECTIVE

Develop infrared (IR) absorption spectroscopic diagnostics for HEDM doped cryogenic parahydrogen (pH₂) solids.

APPROACH

Collect high resolution IR spectra of pH₂ solids doped with <u>non-energetic</u> species: prototypical diatomic, triatomic, linear polyatomic, symmetric top, and spherical top dopant molecules.

Model data as "matrix-perturbed" gas phase spectra, if possible. Develop new spectroscopic models in collaboration with AFRL/Edwards Theory group, as necessary.

SUMMARY

Many, but not all, molecular dopants exhibit very sharp (~0.01 cm⁻¹ FWHM) IR absorption lines in solid pH₂, providing an extremely detailed window into trapping site structures and dynamics.

Model for spherical top molecules trapped in single substitutional sites in fcc and hcp solid pH_2 developed in collaboration with Prof. T. Momose of Kyoto U. is completely successful in explaining spectra of CH_4/pH_2 system. Model of trapped diatomic molecules forthcoming.

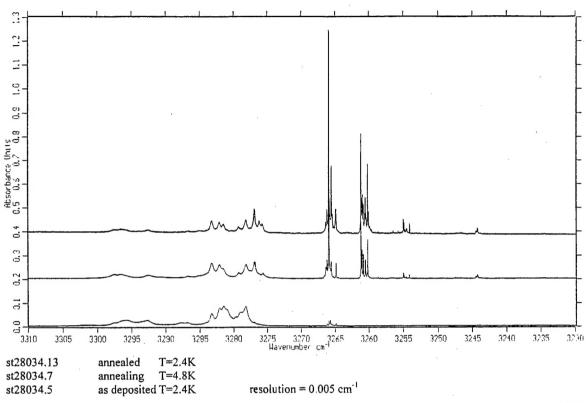
FUTURE DIRECTIONS

Develop model for dopants trapped in multi-substitutional vacancies.

Include effects of lattice relaxation via quantum Monte Carlo methods.

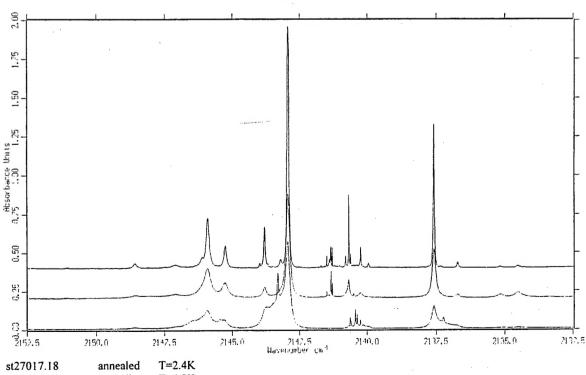
All Dil

9 PPM C_2H_2/pH_2 d≈3mm



ST28004.5

13 PPM CO/pH₂ d≈3mm

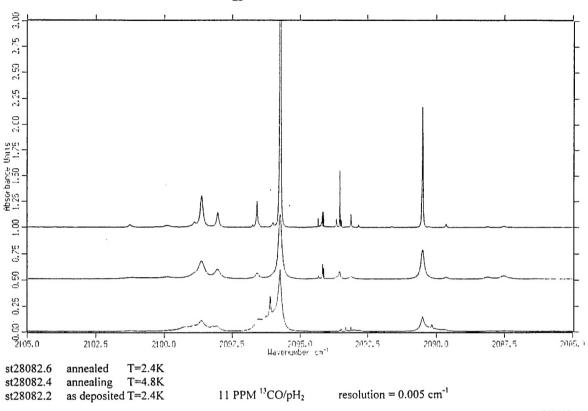


st27017.18 st27017.14 st27017.10 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

resolution = 0.0075 cm^{-1}

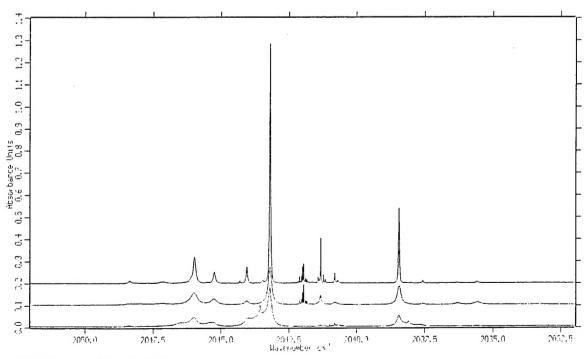
0127017.19

$^{13}C^{16}O/pH_2 d\approx 3mm$



ST28082.2

$^{13}C^{18}O/pH_2 d\approx 3mm$

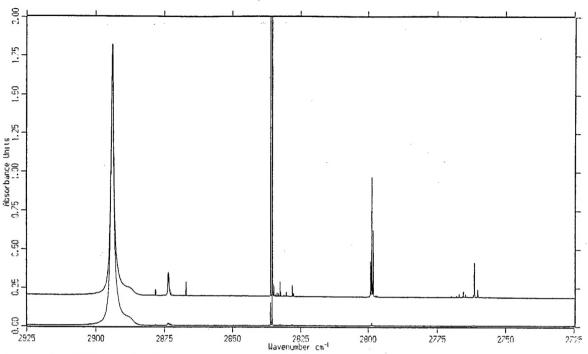


st28085.5 annealed T=2.4K st28085.3 annealing T=4.8K st28085.1 as deposited T=2.4K

29 PPM ¹³CO/pH₂

resolution = 0.005 cm^{-1}

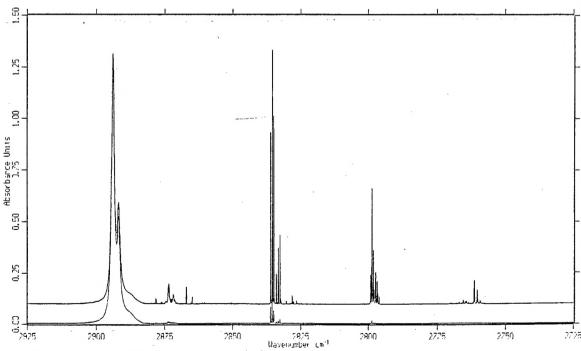
90 PPM H³⁵Cl/pH₂ d≈3mm



st27079.11 annealed T=2.4K st27079.7 as deposited T=2.4K resolution = 0.005 cm⁻¹

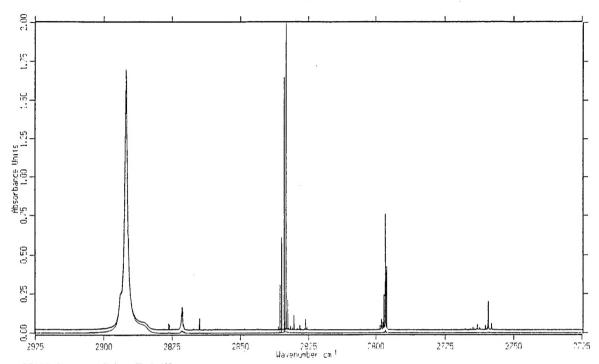
ST27079.7

88 PPM HCl/pH₂ d≈3mm



 $\begin{array}{lll} st27061.11 & annealed & T=2.4K \\ st27061.7 & as deposited & T=2.4K \\ resolution = 0.0075 \text{ cm}^{-1} \end{array}$

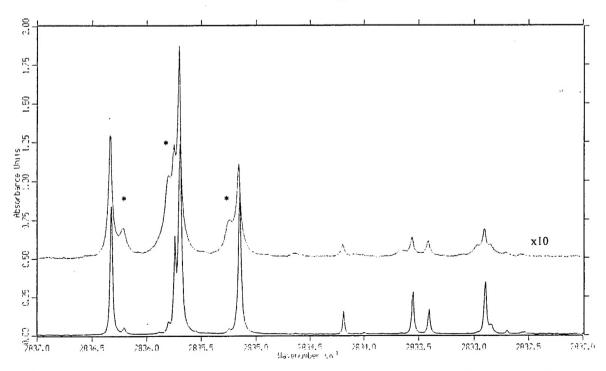
94 PPM H³⁷Cl/pH₂ d≈3mm



st27103.6 annealed T=2.4K st27103.2 as deposited T=2.4K resolution = 0.005 cm⁻¹

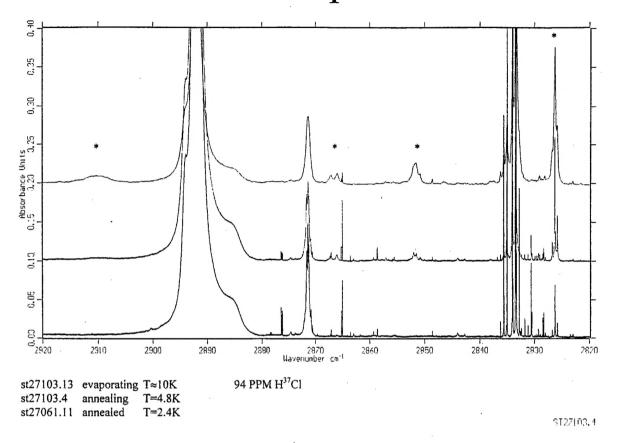
0127103.0

irreversible T dependences

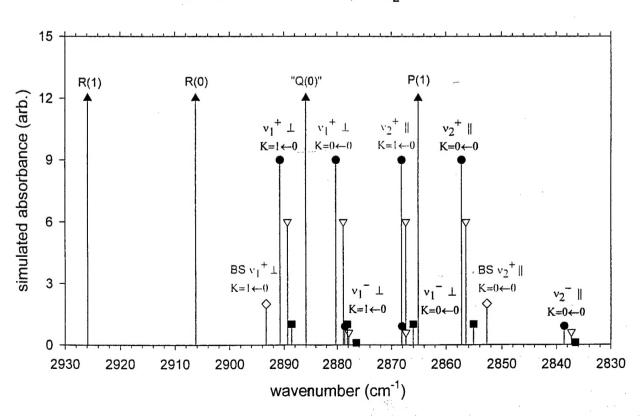


88 PPM HCl/pH₂ d≈3mm st27061.7 as deposited T=2.4K st27061.11 annealed T=2.4K

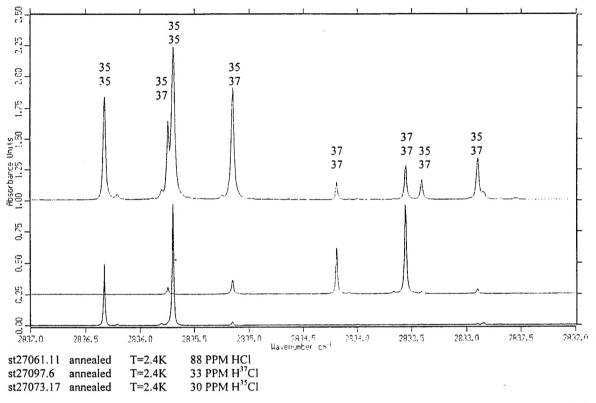
reversible T dependences



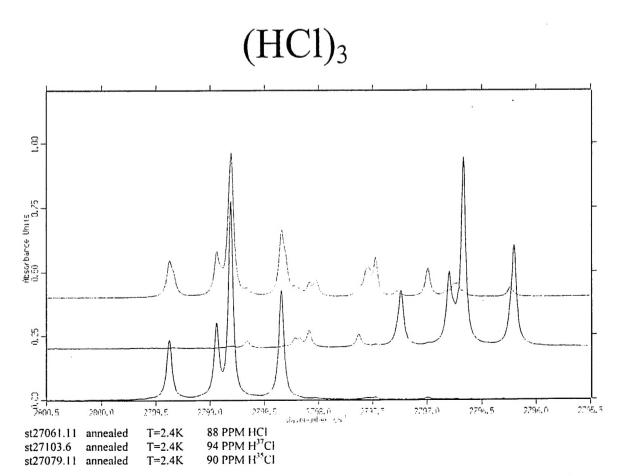
gas phase HCl and (HCl)₂ transitions



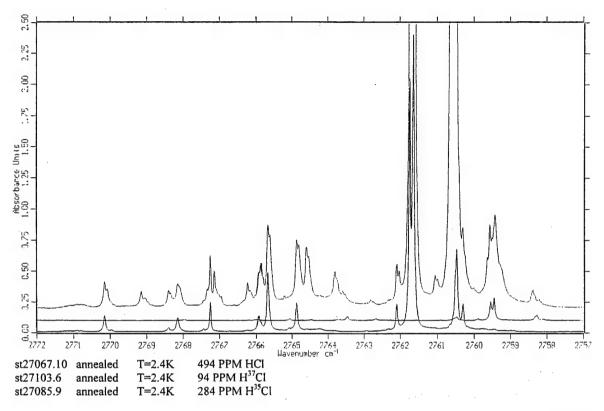
$(HCl)_2 v_2^+$ region



\$127073.17

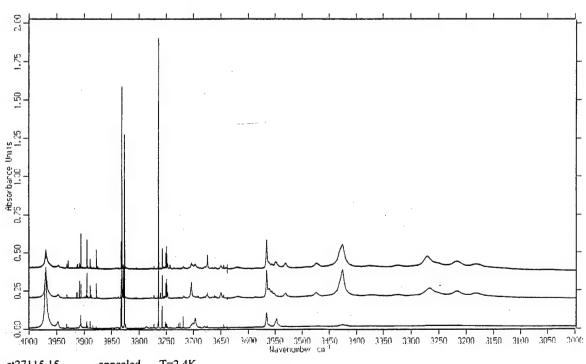


$(HC1)_4$



ST27103.6

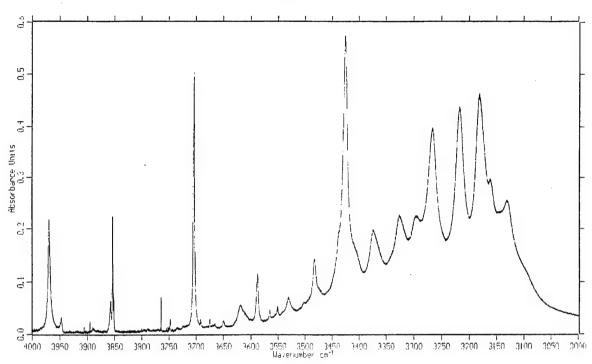
ppm 123 PPM HF/pH₂ d≈3mm



st27115.15 st27115.13 st271215.9 annealed T=2.4Kannealing T=4.8K as deposited T=2.4K

resolution = 0.005 cm^{-1}

$(HF)_n/pH_2$



st27133.15

sample burnoff

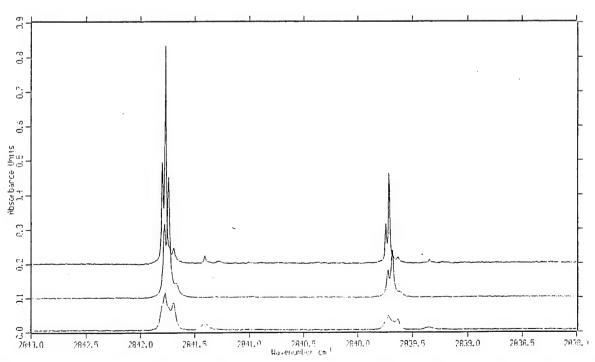
T~10K

268 PPM HF/pH₂

resolution = 0.1 cm^{-1}

9727130.15

HF-HCl/pH₂



st27115.15 st27115.13 st27115.9

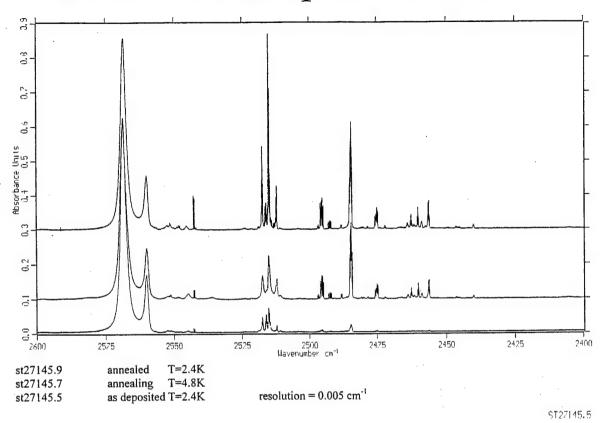
annealed

T=2.4Kannealing T=4.8K as deposited T=2.4K

123 PPM HF/pH₂ d≈3mm

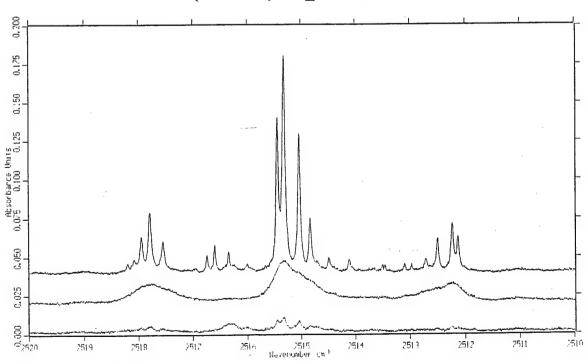
resolution = 0.005 cm $^{-1}$

260 PPM HBr/pH₂ d≈3mm



•

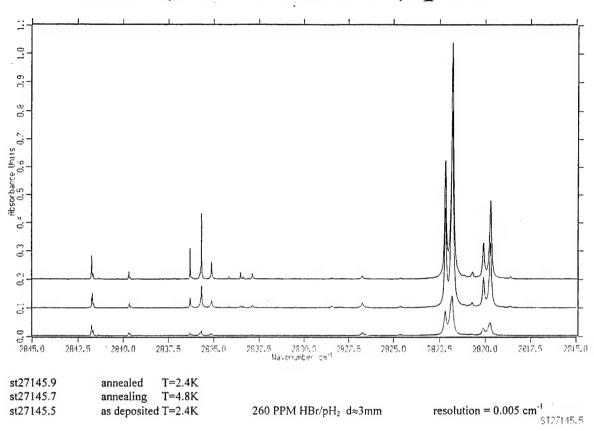
$(HBr)_2/pH_2$



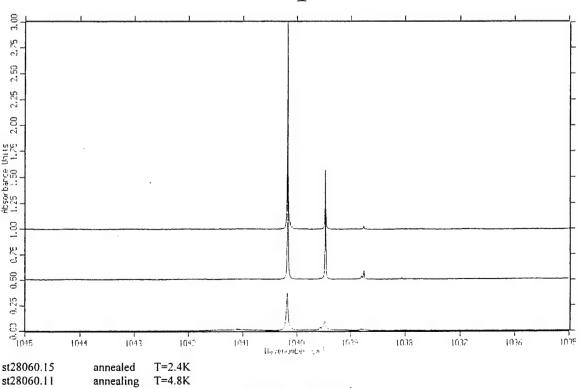
st27140.9 st27140.7 st27140.5 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

80 PPM HBr/pH₂ d≈3mm

HCl-(HF, HCl, HBr)/pH₂



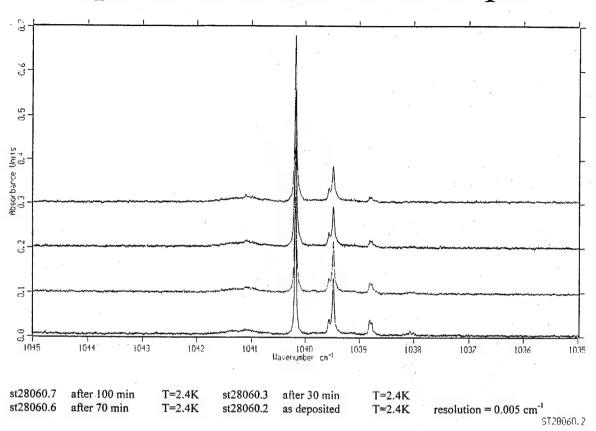
2.4 PPM CH₃F/pH₂ d≈3mm

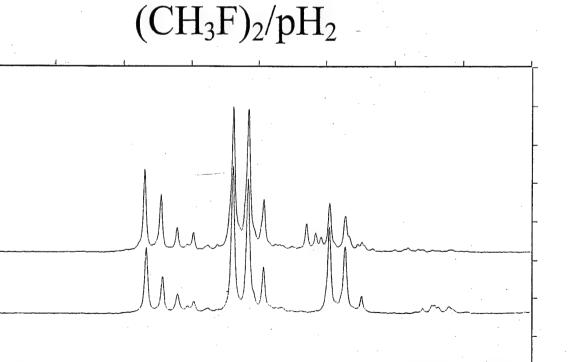


st28060.11 st28060.6+7 as deposited T=2.4K

resolution = 0.005 cm^{-1}

¹H Spin Relaxation in CH₃F/pH₂





1031.25

1031.50

annealing T=4.8K

as deposited T=2.4K

T=2.4K

1031.00 Wavenumber cm

30 PPM CH₃F/pH₂

1936.75

Absorbance Units 0.75 1.00 1.25

JS.

ii:32.00

st28044.11

st28044.7

st28044.3

1031.75

annealed

1030,00

1000.25

1030.50

resolution = 0.005 cm^{-1}

SUPPLEMENTAL MATERIALS

for the poster:

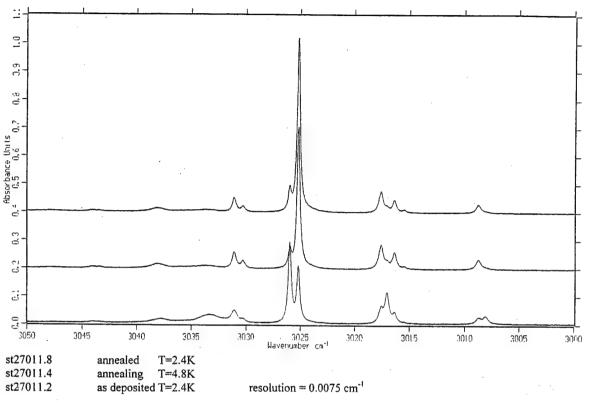
HIGH ENERGY DENSITY MATTER CONTRACTORS CONFERENCE Cocoa Beach, FL 8-11 June 1999

High Resolution Infrared Absorption Spectroscopy of Molecular Dopants in Cryogenic Solid Parahydrogen

Mario E. Fajardo and Simon Tam
US Air Force Research Laboratory, Propulsion Directorate
(AFRL/PRSP Bldg. 8451, Edwards AFB, CA 93524-7680) mario_fajardo@ple.af.mil

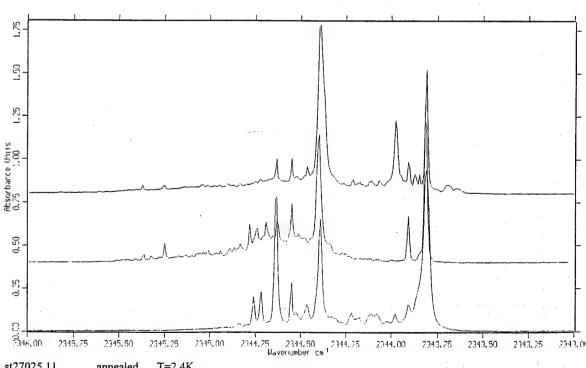
Consisting of spectra of NON-ENERGETIC species trapped in solid hydrogen at low concentrations. These data encompass prototypical diatomic (CO, HCl, HF, HBr), triatomic (CO₂, N₂O, H₂O), linear polyatomic (C₂H₂), symmetric top (NH₃, CH₃F), and spherical top (CH₄) molecular dopants. The basic research activity of understanding these spectra will aid in the future characterization of HEDM cryosolid propellants.

13 PPM CH₄/pH₂ d≈3mm



ST270H.2

1 PPM CO₂/pH₂ d≈3mm

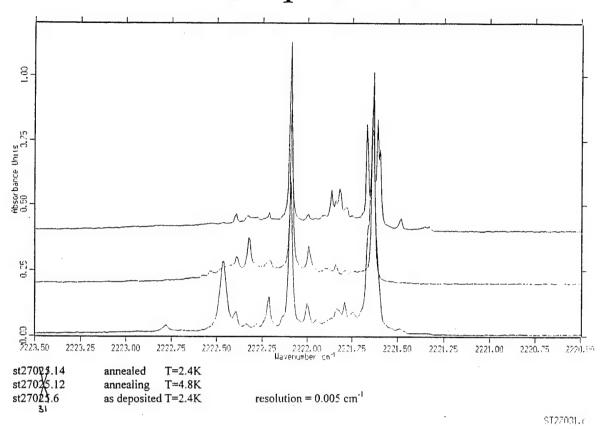


st27025.11 st27025.9 st27025.7 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

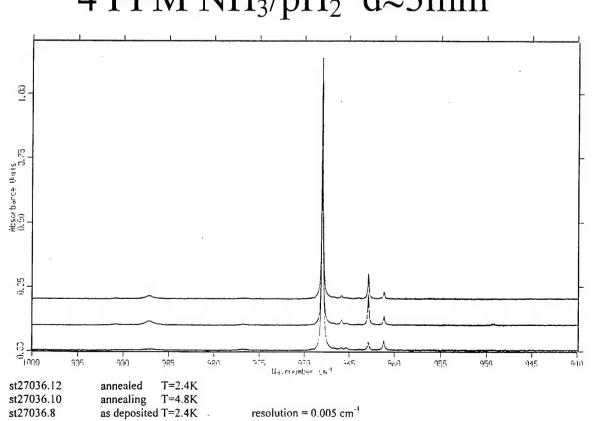
resolution = 0.005 cm^{-1}

ατραμοεί, ο

1-PPM N₂O/pH₂ d≈3mm

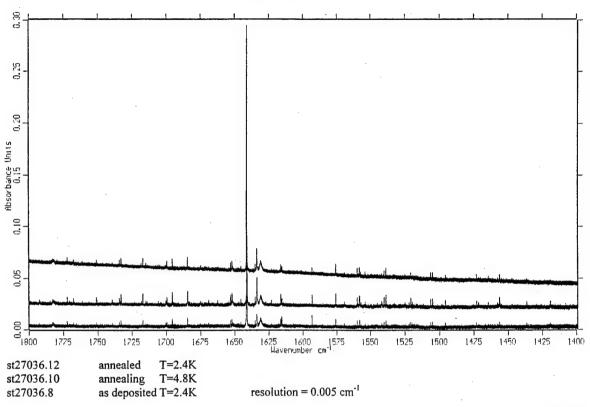


4 PPM NH₃/pH₂ d≈3mm



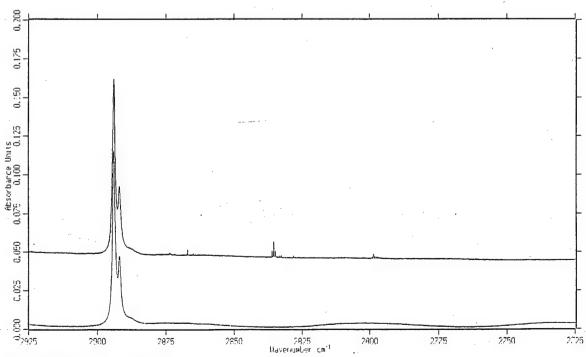
orients.

4 PPM NH₃/pH₂ d≈3mm



ST27036.8

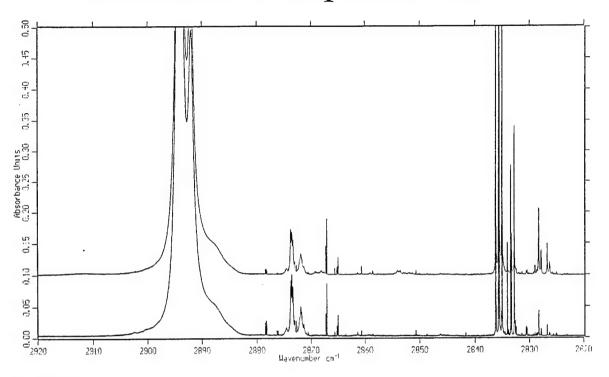
8 PPM HCl/pH₂ d≈3mm



st27055.11 annealed T=2.4K st27055.4 as deposited T=2.4K resolution = 0.05 cm⁻¹

KIDTHEF, A

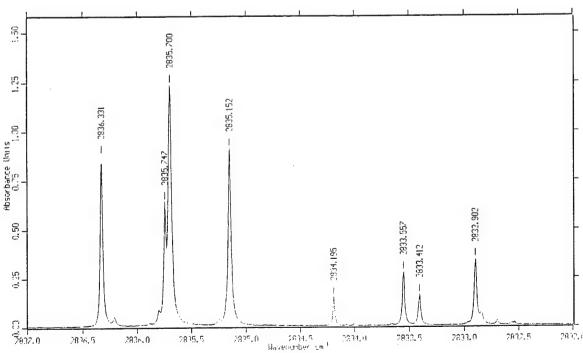
reversible T dependences



88 PPM HCl st27061.9 annealing T=4.8K st27061.11 annealed T=2.4K

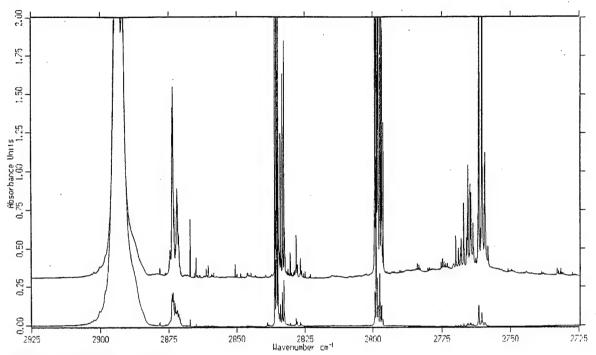
ST27061.9





st27061.11 annealed T=2.4K 88 PPM HCI

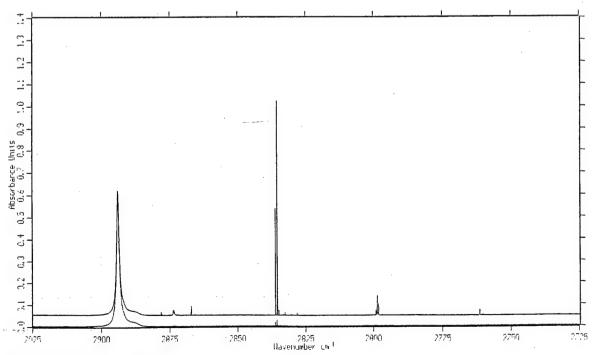
494 PPM HCl/pH₂ d≈3mm



st27067.10 annealed T=2.4K st27067.6 as deposited T=2.4K resolution = 0.0075 cm⁻¹

\$127067.6

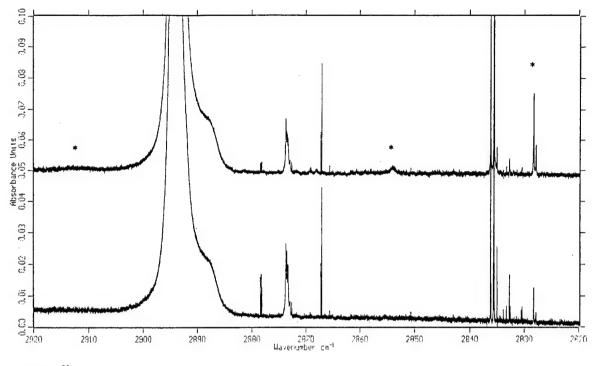
$30 \stackrel{\text{PPM}}{\text{PPM}} \text{H}^{35} \text{Cl/pH}_2 \text{d} \approx 3 \text{mm}$



st27073.17 annealed T=2.4Kst27073.9 as deposited T=2.4Kresolution = 0.005 cm⁻¹

arandan i

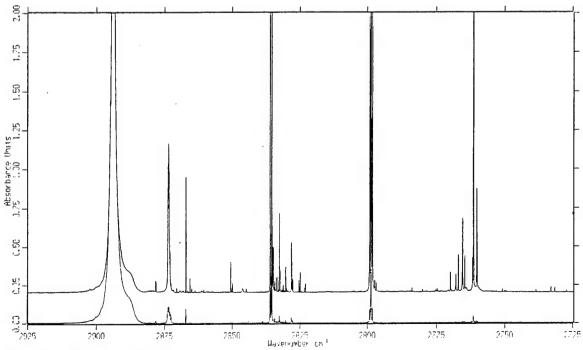
reversible T dependences



30 PPM H³⁵Cl st27073.11 annealing T=4.8K st27073.17 annealed T=2.4K

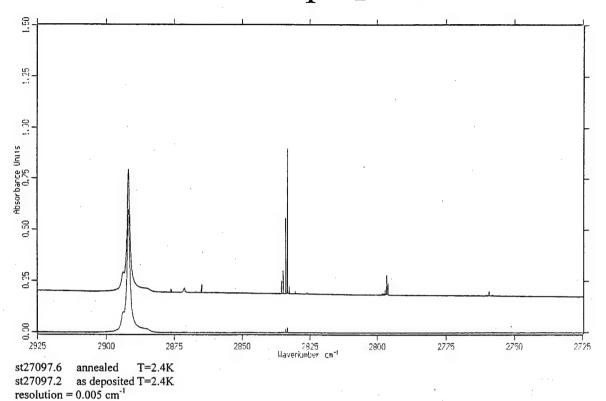
ST27073.11

284 PPM H³⁵Cl/pH₂ d≈3mm



 $\begin{array}{lll} st27085.9 & annealed & T=2.4K \\ st27085.5 & as deposited T=2.4K \\ resolution = 0.005 \text{ cm}^{-1} \end{array}$

$33 \text{ PPM H}^{37}\text{Cl/pH}_2 \text{ d} \approx 3 \text{mm}$

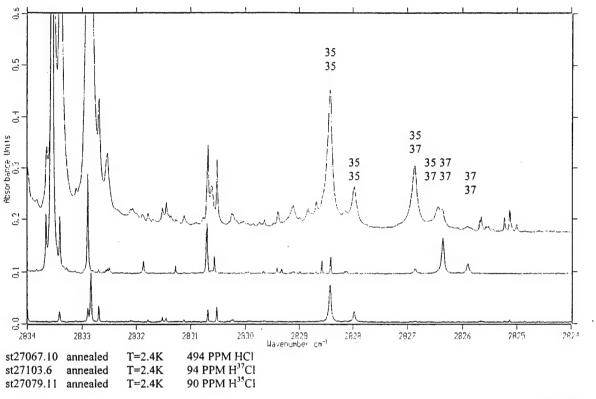


\$127097.2

HCl monomer shifts

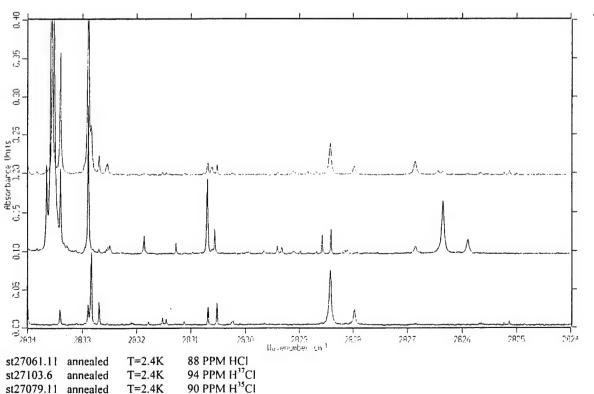
species	line/band	gas phase (cm ⁻¹)	solid pH2	gas-matrix
H ³⁵ Cl	R(1)	2925.8961	2912	14
	R(0)	2906.2464	2894.2	12.1
	"Q(0)"	2885.67	2873.86	
			2873.67	12.0
			2873.46	
			2873.14	
	P(1)	2865.0977	2854.12	
			2853.58	11.5
			2852.95	
H ³⁷ Cl	.R(1)	2923.7315	2910.2	13.5
	R(0)	2904.1104	2892.1	12.0
	"Q(0)"	2883.57	2871.69	
			2871.48	12.1
			2871.31	
			2870.97	
	P(1)	2863.0231	2852.07	, e an esta
			2851.55	11.5
			2850.89	

$(HCl)_2 v_2$ region



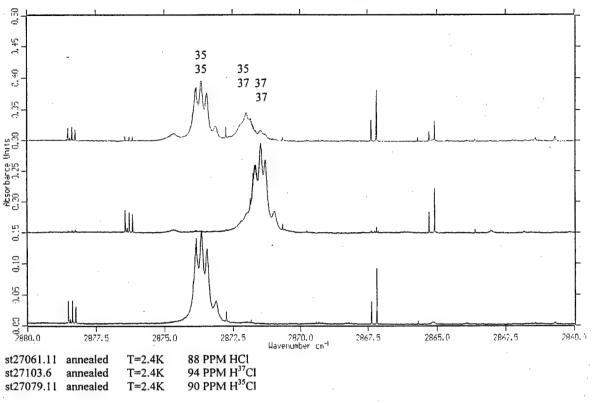
\$122067.10

$(HCl)_2 v_2$ region



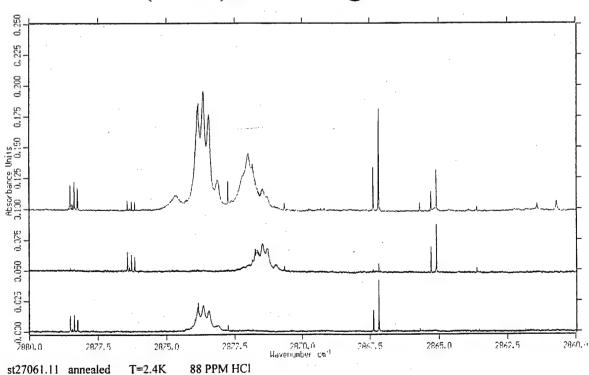
90 PPM H³⁵CI

$(HCl)_2 v_1^+$ region



ST27103.6

$(HCl)_2 v_1^+$ region



st27097.6 annealed

st27073.17 annealed

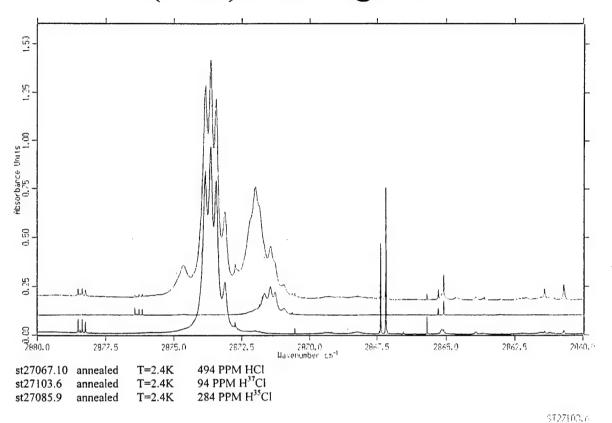
T=2.4K

T=2.4KT=2.4K

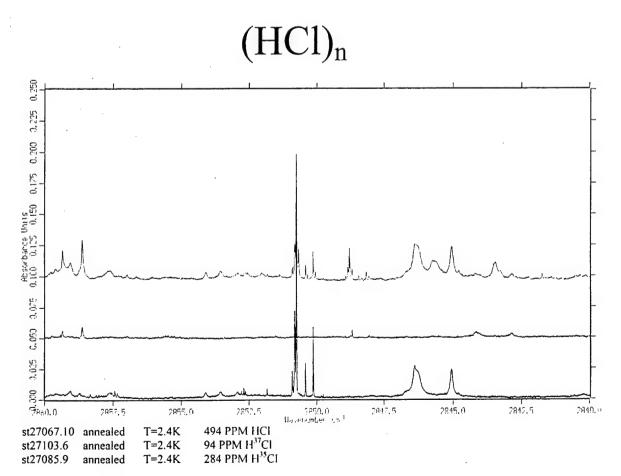
88 PPM HCl 33 PPM H³⁷Cl

30 PPM H35Cl

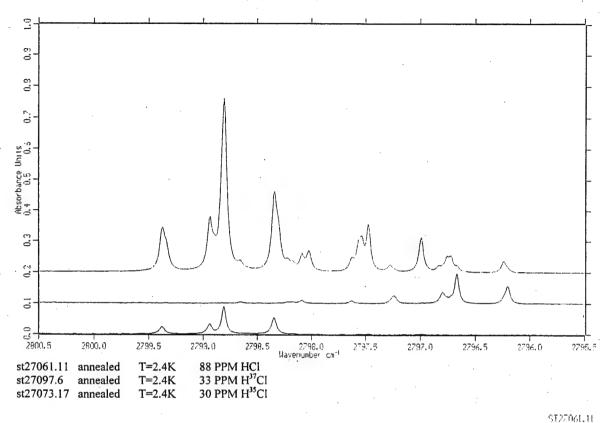
$(HCl)_2 v_1^+$ region



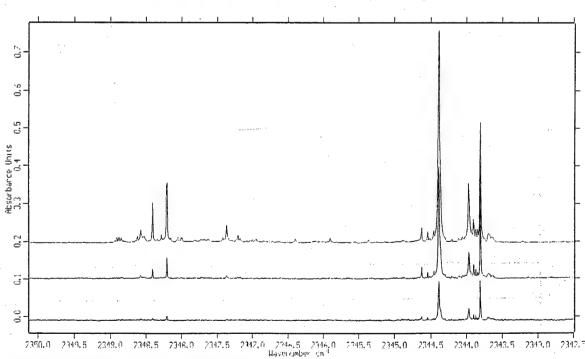




 $(HC1)_3$



v₃ CO₂/(HCl)_n clusters



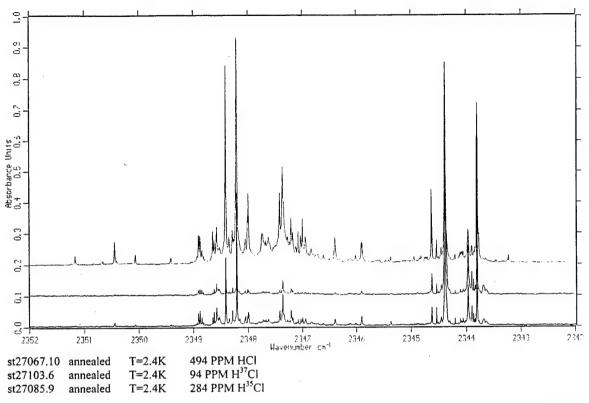
st27061.11 annealed T=2.4K st27097.6 annealed T=2.4K st27073.17 annealed T=2.4K

88 PPM HCl 33 PPM H³⁷Cl 30 PPM H³⁵Cl

0.1.11

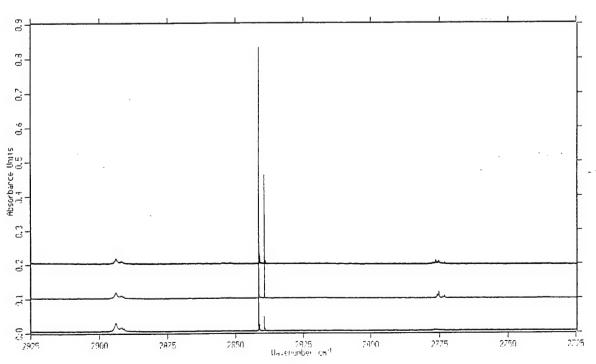
Service To grant and

v₃ CO₂/(HCl)_n clusters



\$127103.7

HF-HCl/pH₂



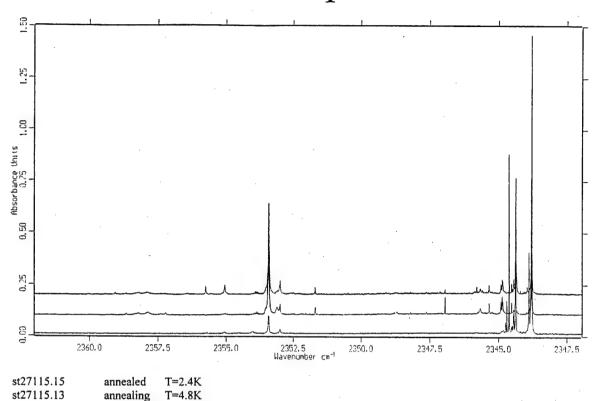
st27115.15 st27115.13 st27115.9

T=2.4Kannealed annealing as deposited T=2.4K

T = 4.8K

123 PPM HF/pH₂ d≈3mm

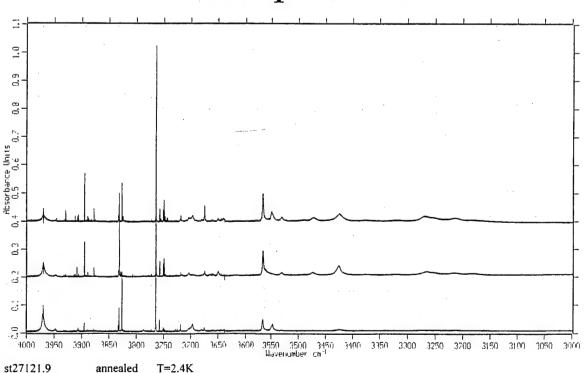
CO₂-HF/pH₂



123 PPM HF/pH₂ d≈3mm

resolution = 0.005 cm^{-1}





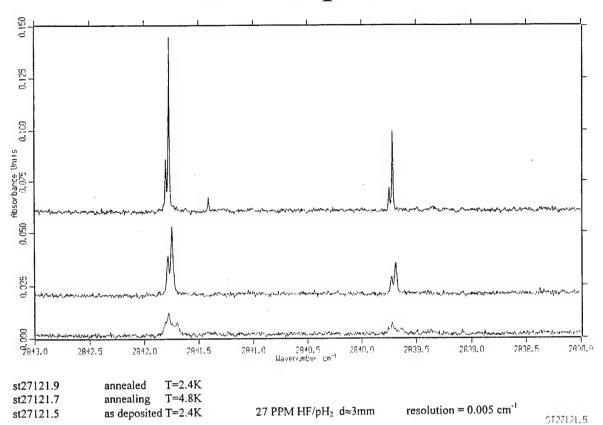
st27121.7 st27121.5

st27115.9

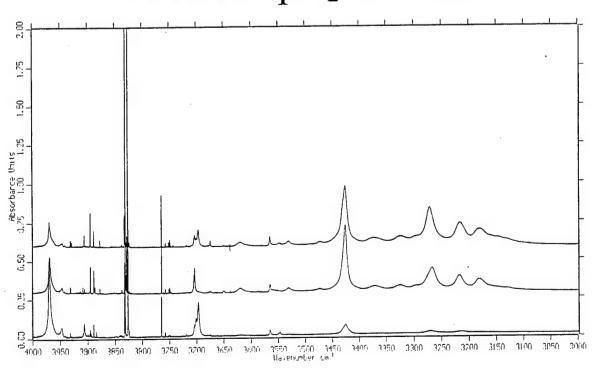
annealed T=2.4K annealing T=4.8K as deposited T=2.4K

as deposited T=2.4K

HF-HCl/pH₂





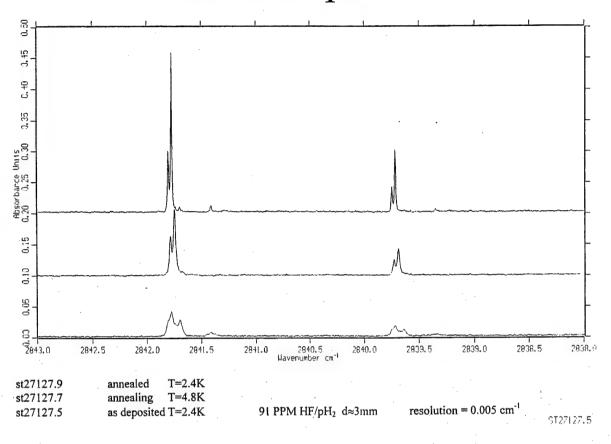


st27127.9 st27127.7 st27127.5 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

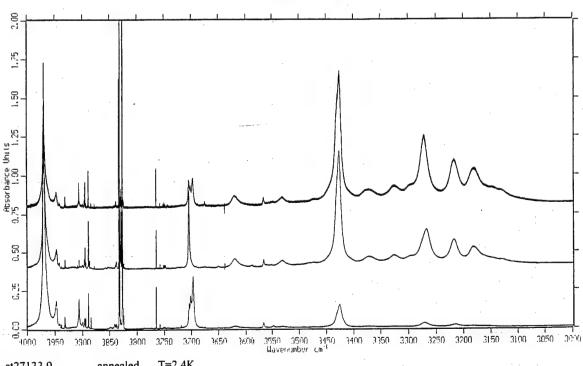
resolution = 0.005 cm⁻¹

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HF-HCl/pH₂



268 PPM HF/pH₂ d≈3mm

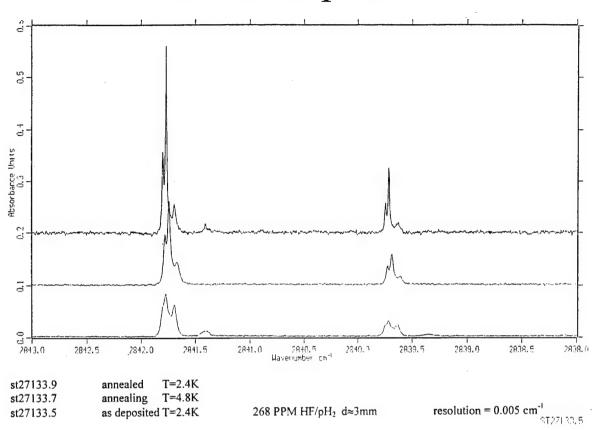


st27133.9 st27133.7 st27133.5 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

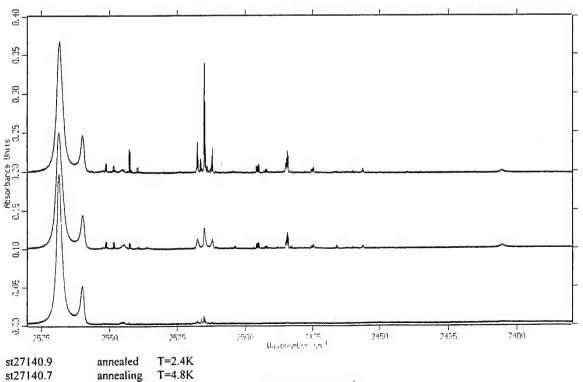
resolution = 0.005 cm⁻¹

0.07[30.0

HF-HCl/pH₂



80 PPM HBr/pH₂ d≈3mm

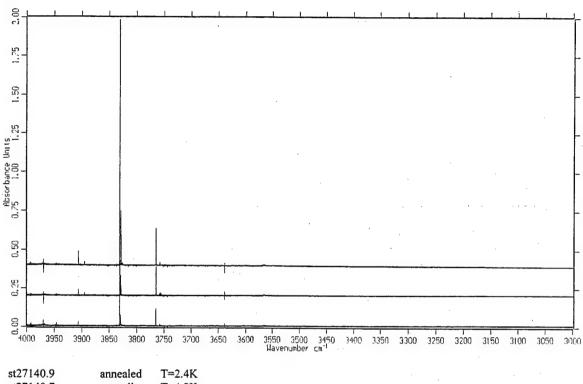


st27140.5

as deposited T=2.4K

resolution = 0.005 cm^{-1}

HF-(HF, HCl, HBr)/pH₂

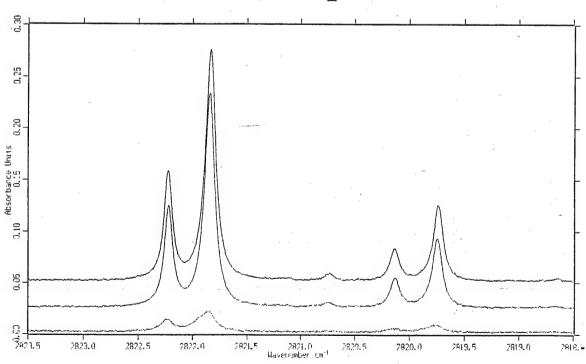


st27140.9 annealed T=2.4K st27140.7 annealing T=4.8K st27140.5 as deposited T=2.4K

80 PPM HBr/pH₂ d≈3mm

resolution = 0.005 cm⁻¹ \$127140.5

HCl-HBr/pH₂

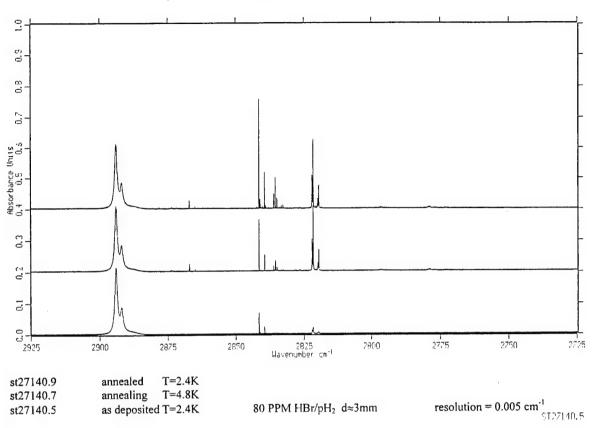


st27140.9 st27140.7 st27140.5 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

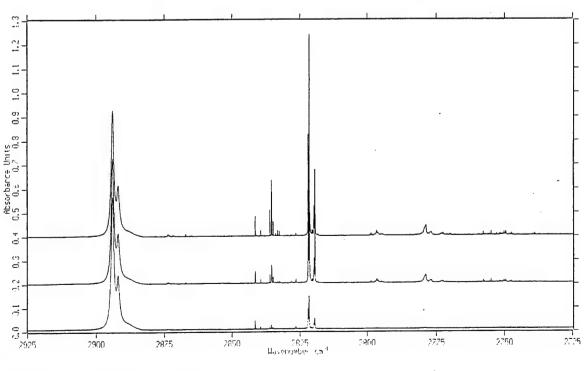
80 PPM HBr/pH₂ d≈3mm

resolution = 0.005 cm^{-1}

HCl-(HF, HCl, HBr)/pH₂



HCl-(HF, HCl, HBr)/pH₂

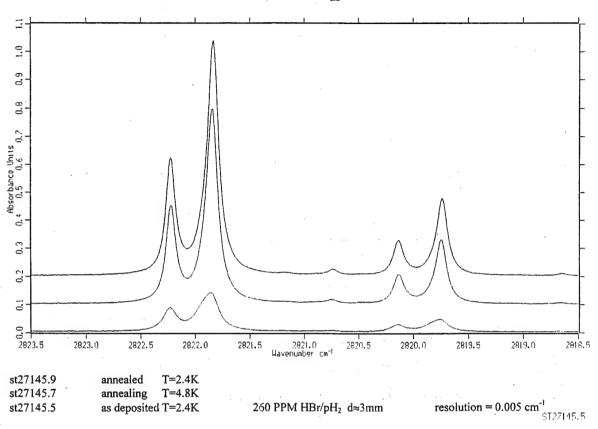


st27145.9 st27145.7 st27145.5 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

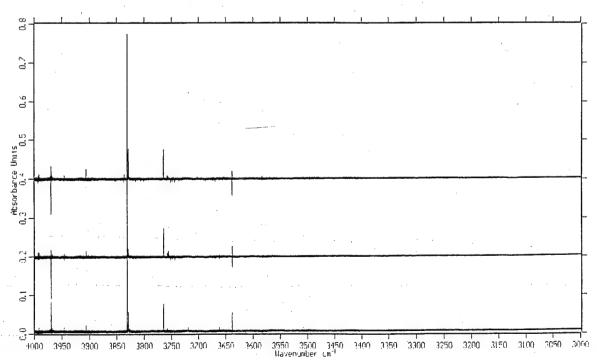
260 PPM HBr/pH₂ d≈3mm

resolution = 0.005 cm⁻¹ r_{constant}

HCl-HBr/pH₂



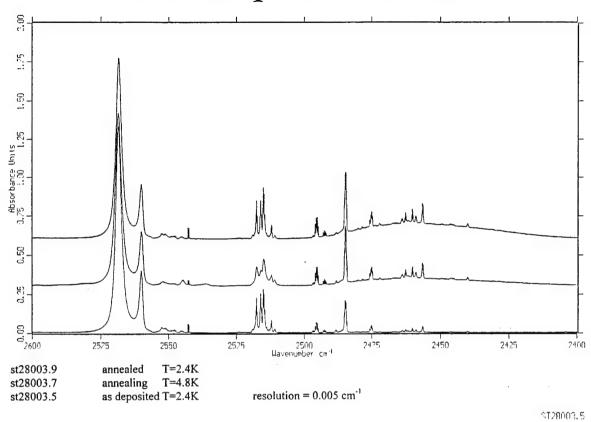
HF-(HF, HCl, HBr)/pH₂



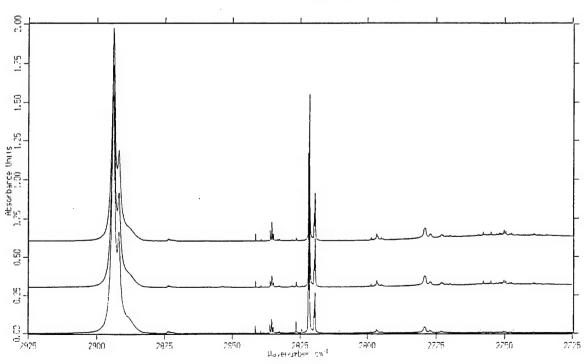
st27145.9 st27145.7 st27145.5 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

260 PPM HBr/pH₂ d≈3mm

645 HBr/pH₂ d≈3mm



$HCl(HBr)_n/pH_2$



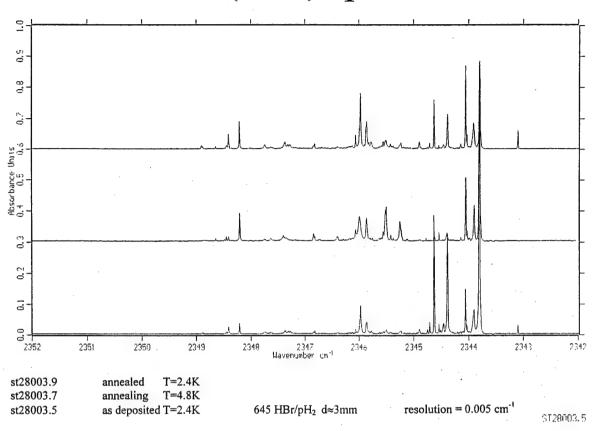
st28003.9 st28003.7 st28003.5 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

645 HBr/pH₂ d≈3mm

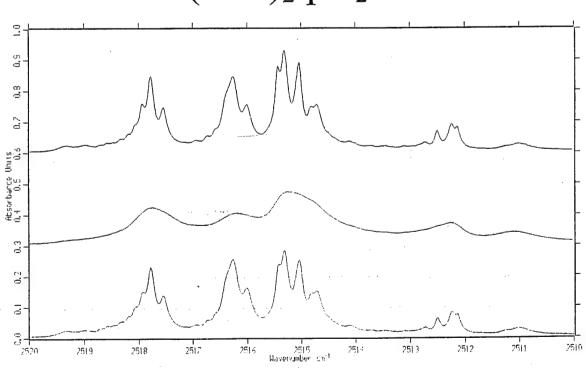
resolution = 0.005 cm^{-1}

7280e9. n

$CO_2(HBr)_n/pH_2$



$(HBr)_2/pH_2$



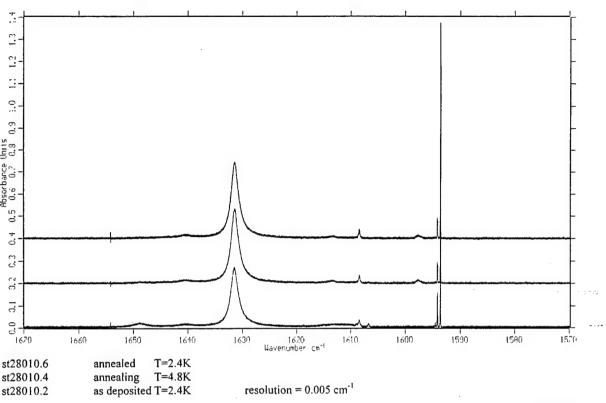
st28003.9 st28003.7 st28003.5 annealed T=2.4K annealing T=4.8K as deposited T=2.4K

645 HBr/pH₂ d≈3mm

resolution = 0.005 cm⁻¹

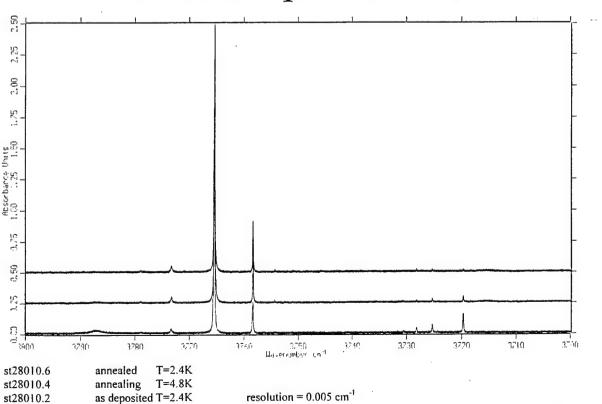
 $\eta T/\Omega (000) T$

15 PPM H_2O/pH_2 d≈3mm



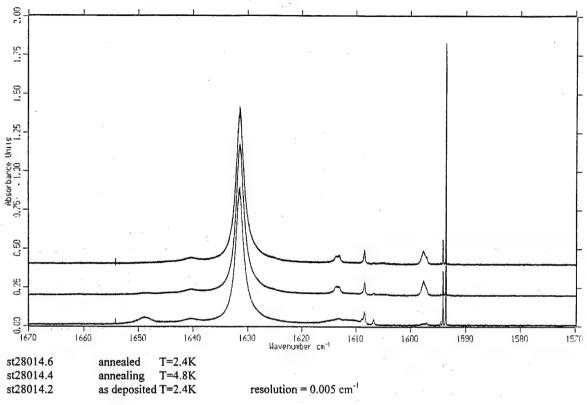
ST28010.2

15 $\stackrel{\text{ppm}}{\text{PPM}}$ H₂O/pH₂ d≈3mm



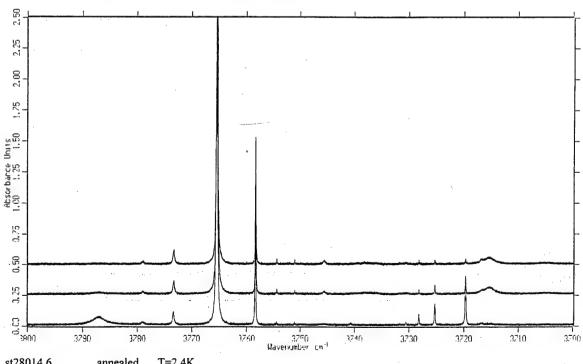
resolution = 0.005 cm^{-1}

45 PPM H₂O/pH₂ d≈3mm



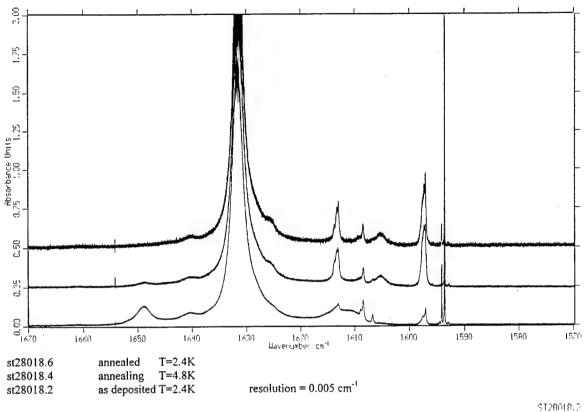
ST28014.2

45 PPM H₂O/pH₂ d≈3mm

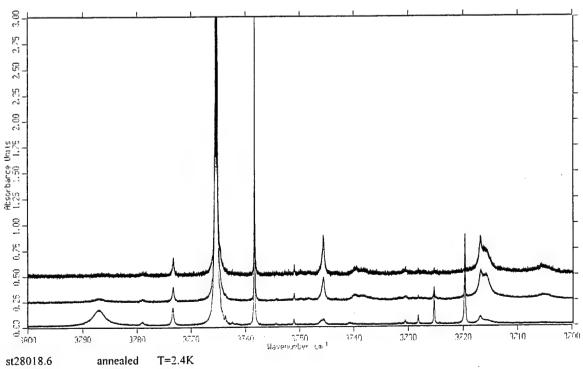


st28014.6 st28014.4 st28014.2 annealed T=2.4K annealing T=4.8Kas deposited T=2.4K

138 PPM H_2O/pH_2 d≈3mm



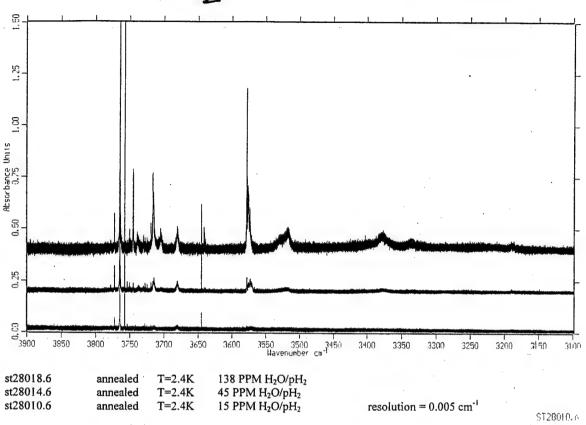
138 PPM H₂O/pH₂ d≈3mm



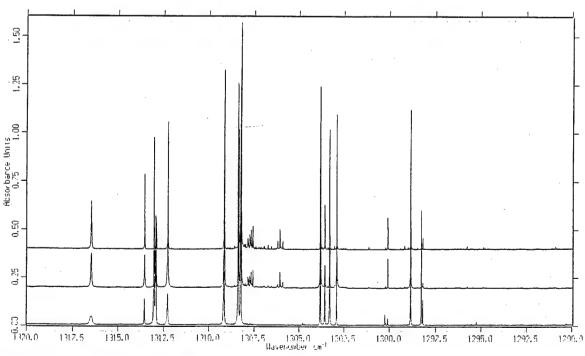
st28018.4 st28018.2

T=4.8Kannealing as deposited T=2.4K

H₂O clusters in pH₂



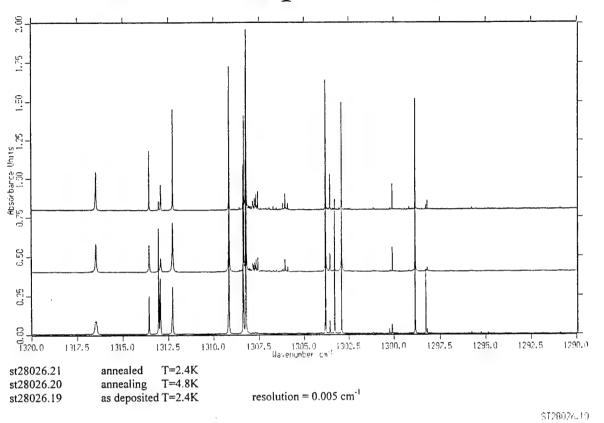
56 PPM CH₄/pH₂ d≈0.7mm



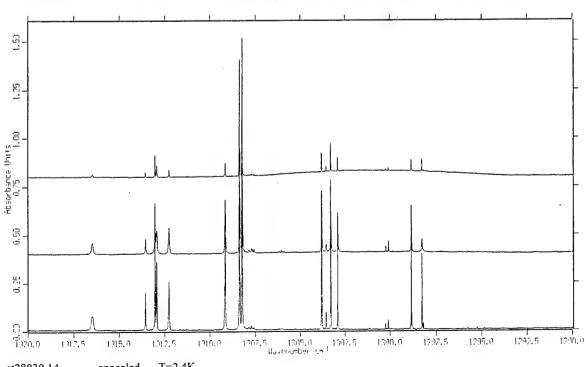
st28022.20 st28022.19 st28022.18 annealed T=2.4K annealing T=4.8K

annealing T=4.8K as deposited T=2.4K

200 PPM CH_4/pH_2 $d\approx 0.2mm$



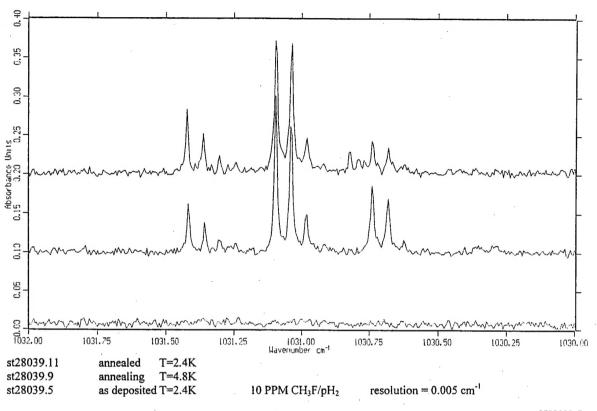
550 PPM CH₄/pH₂ d≈0.05mm



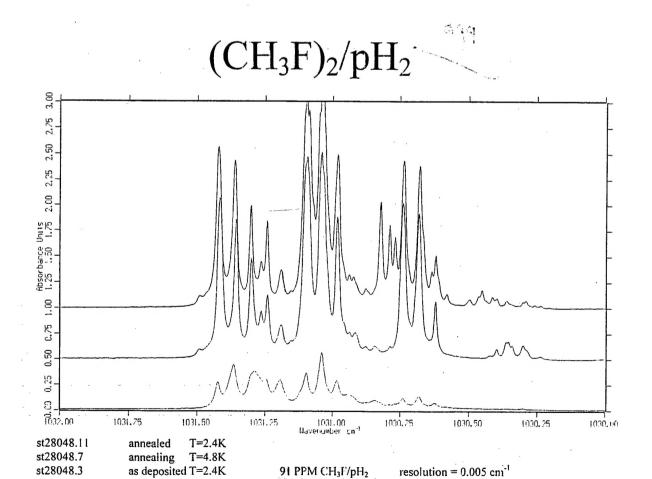
st28030.14 st28030.13 st28030.12 annealed annealing

T = 2.4KT=4.8Kas deposited T=2.4K

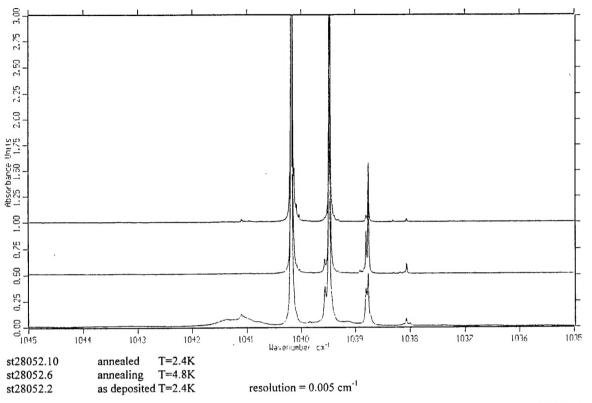
$(CH_3F)_2/pH_2$



ST28039.5

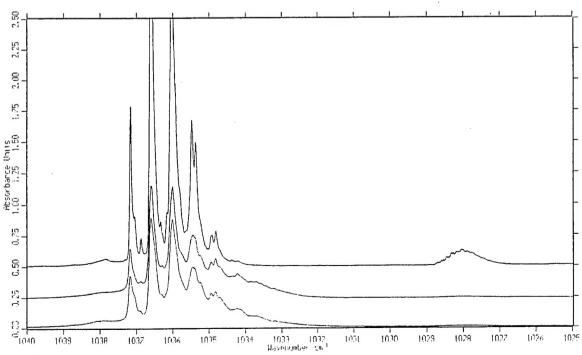


6 PPM CH₃F/pH₂ d≈3mm



\$128052.2

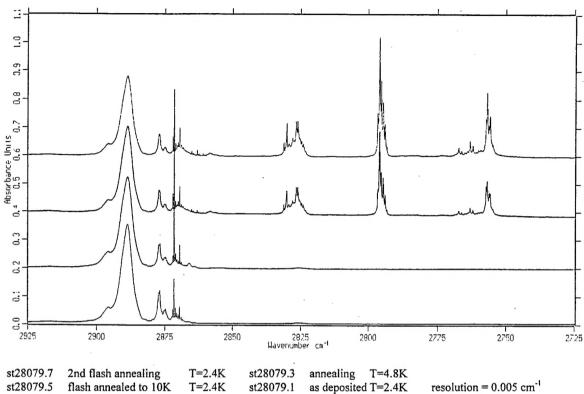
33 PPM CH₃F/oD₂ d≈2mm



st28073.11 flash annealed to 10K st28073.7 annealing T=4.8K

st28073.7 annealing T=4.8K st28073.3 as deposited T=2.4K T=2.4K

93 PPM HCl/oD₂ d≈2mm



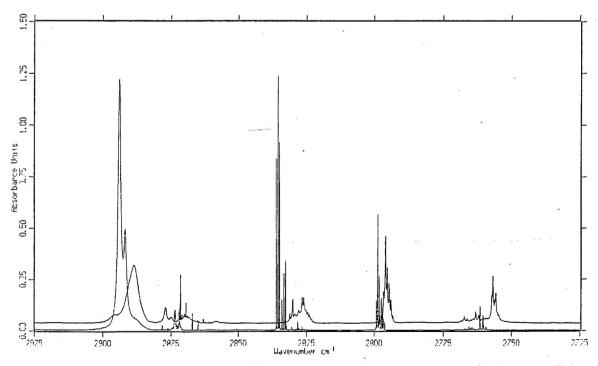
flash annealed to 10K

T=2.4K

resolution = 0.005 cm^{-1}

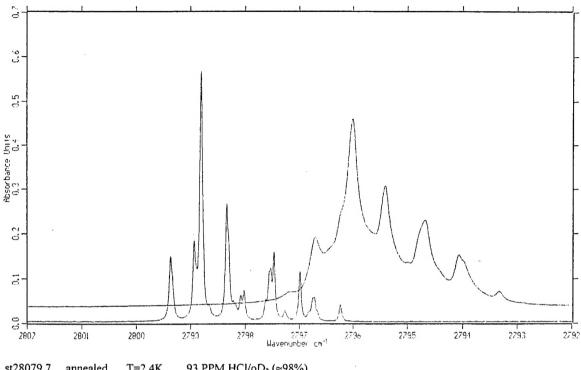
ST28079.1

HCl/pH₂ vs. HCl/oD₂



st28079.7 annealed st27061.11 annealed T=2.4KT=2.4K 93 PPM HCl/oD₂ (≈98%) 88 PPM HCl/pH2 (99.99+%)

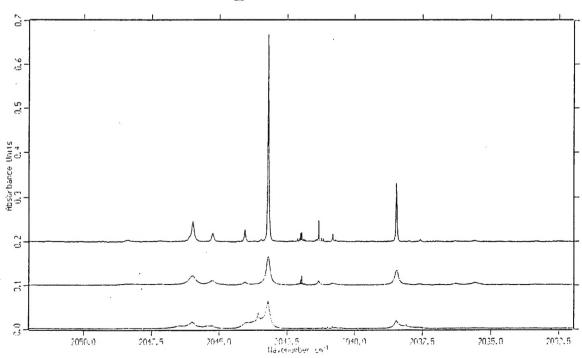
$(HCl)_3/pH_2 & (HCl)_3/oD_2$



st28079.7 annealed T=2.4K 93 PPM HCl/oD₂ (≈98%) st27061.11 annealed T=2.4K 88 PPM HCl/pH2 (99.99+%)

\$127061.11

$^{13}C^{18}O/pH_2 d\approx 3mm$



st28082.6 a

annealed T=2.4K annealing T=4.8K

st28082.4 annealing T=4.8K st28082.2 as deposited T=2.4K

BK BK 11 PPM ¹³CO/pH₂

resolution = 0.005 cm^{-1}